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EFFECT OF FUEL ADDITIVES STUDY

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Michigan University

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EFFECT OF FUEL ADDITIVES STUDY

by

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SUMMARY

We have carried out studies to be published in Analytical Chemistry on the optimization of a chemiluminescent NO detector. This detector has been used to study the effect of N containing fuel additive combustion using a gas chromatographic technic. Progress so far indicates N selective GC detection down to 1.6 ng of diethyl nitrosamine (~0.5 ppm in a 1 ml gas sample). Similar data are obtained for amines. The detector has at least two orders of magnitude more sensitivity currently not realised due to problems with the GC columns.

Preliminary studies have been made of rapid determination of total N in gasoline, and of combustion products in a flat flame propane-air burner.

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16. ABSTRACT

Studies were carried out on the optimization of a chemiluminescent NO detector. This detector has been used to study the effect of N containing fuel additive combustion using a gas chromatographic technique. Progress so far indicates N selective GC detection down to 1.6 ng of diethyl nitrosamine (~0.5 ppm in a 1 ml gas sample). Similar data are obtained for amines. The detector has at least two orders of magnitude more sensitivity currently not realized due to problems with the GC columns.

Preliminary studies have been made of rapid determination of total N in gasoline, and of combustion products in a flat flame propane-air burner. (Author summary modified).

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PRICES SUBJECT TO CHANGE

Introduction

The overall goal of this research, as outlined in the original proposal, was to develop and apply analytical techniques to determine combustion products arising from two gasoline fuel additives: disalicylidene propane diamine (Universal Oil Products 55) and NC_{15} alkenyl succimide (sic)(Lubrisol 580). Specifically,this meant developing and adapting a chemiluminescent NO detector as a nitrogen specific gas chromatography detector sensitive enough to measure ppm concentrations of either additive or combustion products, and using the detector to look for these products when these additives were added to the fuel of either a flat flame burner or an automobile engine.

The sequence of experiments were to be as follows: 1.) Carry out some physical and chemical tests on the two fuel additives supplied by EPA. 2.) Build and optimize a chemiluminescent NO detector. 3.) Develop the detector as a N specific G.C. detector. 4.) Establish the limits of detectibility of the instrument for several N containing compounds. 5.) Develop techniques for adding ppm quantities of fuel additive to the propane fuel of a flat flame burner and sampling the possible combustion products for analysis with the G.C. and the new detector. 6.) Repeat 5.) with a propane fueled single cylinder engine. 7.) If warranted by the results of 5.) and 6.), extend the measurements to a multicylinder gasoline fueled engine. As will be shown in the report, we have successfully accomplished steps 1.) - 3.), and have done a great deal towards

finishing 4.) and 5.), but certain difficulties remain, and some new approaches are being tried to improve the detector and the burner experiments.

Fuel Additives

As it turned out, the two fuel additives supplied for this project were chemically bad choices for analytical research using gas chromatography. Their particular disadvantages will be discussed separately.

Lubrizol 580, originally identified to us as NC_{15} alkenyl succimide, is a product of a condensation reaction of maleic anhydride and polybutylene amine, where the polybutylene amine is a C_{50} hydrocarbon with a single amine group on the end (1). The product polymer undoubtedly is a mixture of several adducts with the final formulation containing 0.8% N by weight (1). The additive is supplied commercially as a mixture of polymer, xylenes, a long chain alcohol, and an emulsifier (1).

The above information was confirmed by a simple column chromatography separation of Lubrizol 580 and taking nmr spectra of the separated constituents. The polymer accounts for 70% by weight of the mixture, while the alcohol is 15% by weight.

The polymer has not been found to pass through any gas chromatograph, and would not volatilize below 340°C. Therefore, with Dr. Ronald Bradow's permission, we abandoned any further work with Lubrizol 580 and concentrated our effort on the other additive.

N,N -Disalicylidene-1,2-propanediamine, also known as salicyl propanediamine, or α,α'-(propylenedinitrilo)-di-o-cresol was

originally represented to us as a sample of a Universal Oil Products fuel additive, UOP-55, but a request for more of the additive is found in a number of applications, for instance DuPont Metal Deactivator. It seems the compound is a well-known metal chelating agent which is supplied dissolved in an appropriate organic solvent. We have recrystallized it from cold heptane and used the pure crystals to make up known solutions in benzene. Our purified sample had a melting point of 38-40°C, and the nmr spectrum agreed generally with the expected structure, but there was an absorbance at ∿13 ppm, presumably due to the double bond hydrogen, that looks more like it is bonded directly to the nitrogen. A high resolution mass spectrum of the compound had a large parent peak at about mass 280 (expected 284) and the mass fractions were consistent with the expected structure.

The problem with this additive stems from its chelating ability and subsequent strong affinity for metal surfaces. On glass or ceramic material the compound vaporized at an appreciable rate at approximately 85°C. On stainless steel, temperatures on the order of 220-250°C were required before any appreciable amount disappeared. Since the burner, the inlet system of the G.C., the G.C. columns, and part of the gas sampling valve are all metal, considerable difficulty has been encountered in finding a gas chromatographic system that will pass the additive.

On the basis of the gas chromatography literature four matched pairs of six foot stainless steel G.C. columns were made for separating amines: 5% polyethylene imine on Chromsorb G, 5% Versamid 900 on Chromsorb G, 5% Triton X-100 on Chromsorb G, and Chromsorb 103. Using several primary and secondary amines from Polyscience Corporation Qual-Kits (98% + purity) it was found that all of these columns

separate amines with negligible tailing. The Chromsorb 103 column was good with low molecular weight amines, while the others seem to be better with higher molecular weights.

The only column that would pass pure disalicylidene propanediamine was the polyethylene imine column at 240°C with the injector at 300°C. Under these conditions, however, there is considerable background bleed of the liquid phase imine that is picked up by the N specific detector, and this column is not suitable to detect the additive or its combustion products at ppm levels. In fact no column with a liquid phase molecule which contains one or more N atoms can be used unless column temperatures are kept well below maximum levels. Thus the Versamid 900 column was also unsatisfactory.

The Chromsorb 103 polymer contains no nitrogen, but it only passed low molecular weight amines easily. Furthermore 50 ppm NO in nitrogen when injected as a 1cc gas sample disappeared on this column. Therefore it did not seem to be promising as an analytical system dealing with nitrosoamines and large molecular weight fragments from the fuel additive.

This left only the Triton X-100 column, which did separate low molecular weight amines and nitrosoamines satisfactorily, and by itself caused quite low background levels on the detector. The problem here is that the temperature limit for the column is 200°C, and the additive will not go through a stainless steel column at that temperature. We tried to saturate the metal surfaces by continuously injecting a 1% solution of the additive in benzene into the G.C. at about 3 µl/min for 4-5 hours and under these conditions the additive was detected,

but once continuous injection was stopped 1 µl injections of the 1% solution were not getting through to the detector.

Two columns which are both 5% Triton X-100 on Chromsorb G have been made. In addition one column also has 5% KOH on it and the other 5% "Desicote" (a Beckman Instruments, Inc. silicone solution), and the stainless steel tubing for the column was thoroughly washed on the inside with a 1% benzene solution of the disalicylidene propanediamine additive. Unfortunately, instrument problems have prevented testing the ability of these new columns to pass the additive by the time this report was written.

The inability of finding a column that will pass the parent additive to the detector has been frustrating, and makes development of injection and sampling techniques with the flat flame burner very difficult. What might work well for lower molecular weight amines and nitrosoamines might be unsatisfactory for the high molecular weight additives and their combustion products.

Chemiluminescent NO Detector

The construction and optimization of the chemiluminescent NO detector with a limit of NO detectibility of at least 10 ppb has been covered in a preliminary report to EPA last fall. The experiments that examined the ideal operating parameter and reactor design led to a paper, which was submitted to Analytical Chemistry, and has now been accepted for publication. A preprint of that paper has been included with this report, and one can refer to it for complete descriptions of the detector, reactor, and operating parameters utilized in these experiments. **(Appendix I)**

A Nitrogen Specific G.C. Detector

Perhaps the most important contribution of this research has been the successful development of the NO detector as an N specific detector for gas chromatography. The experimental design is as follows.

For these experiments, the G.C. was a Perkin-Elmer model 800 with dual flame ionization detectors with output to both a 10 milivolt strip chart recorder and an Infotronics Corp. CRS-10H digital integrator. Samples could be introduced with either a Carle gas sampling valve or Hamilton liquid or gas syringes. The normal entrance to the flame ionization detector was blocked. As shown in Figure 1, all of the effluent from the column, in 1/8 inch stainless steel tubing, passed into a 1/8 inch Swagelok tee where it met a stream of pure oxygen and passed immediately into the conversion furnace.

The conversion furnace was 6-7 inches of 1/8 inch stainless steel tubing which was wrapped with about six feet of 32 gauge nichrome wire (10.58 ohms/ft resistance) over a thin layer of asbestos tape. Another layer of asbestos was wrapped over the wire and a thin layer of Sauereisen was applied over the whole furnace. A chromel-alumel thermocouple had been placed near the middle of the furnace between the tubing and the first asbestos layer. The nichrome wire was connected to a Variac, and the furnace produced a linear range of temperatures from 450 to 950°C for Variac settings of 58 to 108 volts. About two feet of platinized (from chloroplatonic acid) platinum wire was folded up and inserted into the stainless steel tubing to serve as a catalyst for the conversion of all the nitrogen atoms in

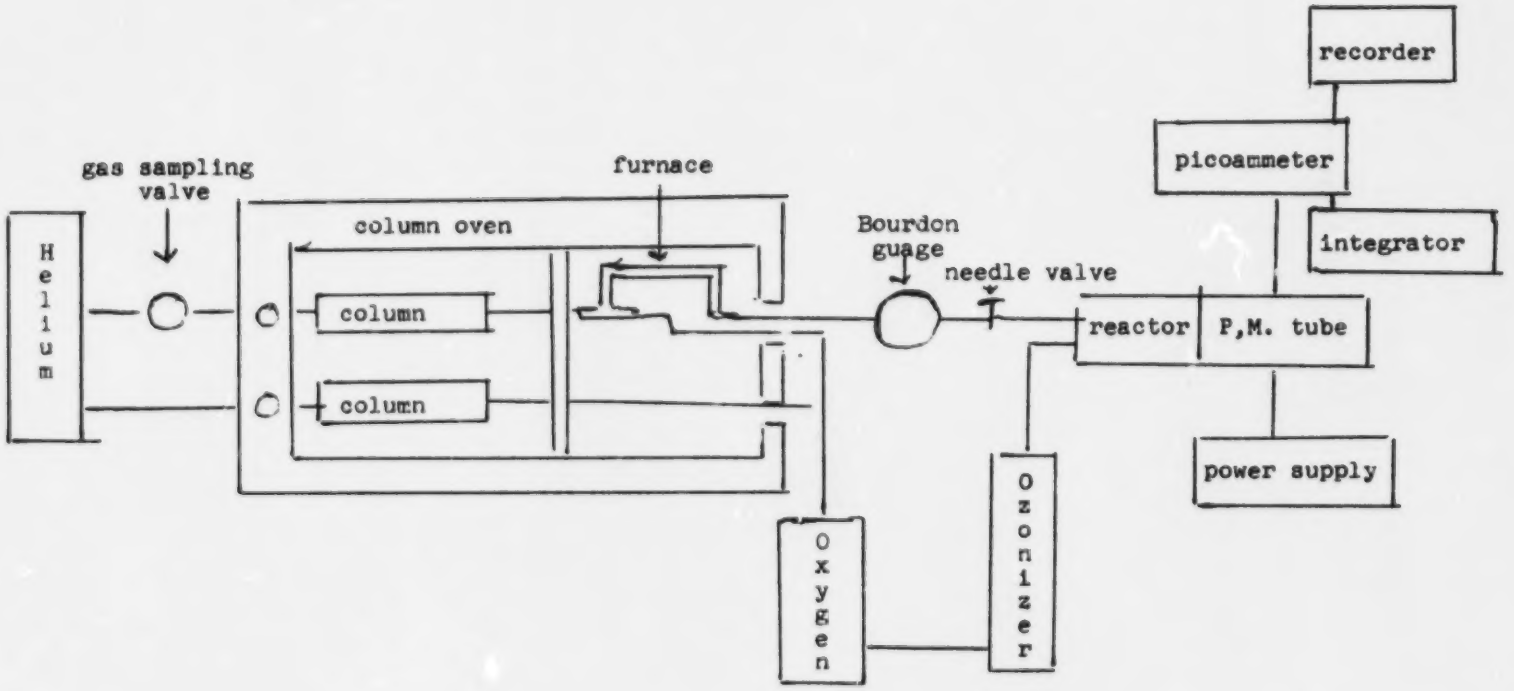

Figure 1. Block diagram of the gas chromatograph, conversion furnace, and chemiluminescent NO detector.

the effluent molecules to NO, the thermodynamically stable oxide of nitrogen at 800-900°C.

The actual location of the furnace in the column oven is shown in Figure 1. The products from the furnace are carried in the 1/8 inch stainless steel tubing through a Bourdon tube vacuum-pressure gauge (Marsh Instrument Company), a needle valve, and then connected to the black Tygon inlet tubing of the reactor of the NO detector. In addition to being displayed on a 10 millivolt recorder, the output signal from the NO detector (now the G.C. detector) was also put into the digital integrator.

The system worked beautifully as a G. C. detector. For a variety of primary amines, secondary amines, and several nitrosoamines, the detector produced nice Gaussian peaks over a wide range of sample concentrations. For example, Figure 2 shows a sample chromatogram for a mixture of three primary amines, and Figure 3 shows two chromatograms of the same mixture of diethylamine and N-nitrosodiethylamine where the amine concentrations differs by at least 10^4 in the sample injected into the G. C. Clearly the detector ignores the benzene solvent, but responds as one would expect of a G. C. detector for the amine compounds.

As soon as it was clear that the NO detector and conversion furnace would make a satisfactory G. C. detector a number of experiments were carried out to determine the critical operating parameters for the detector and hence the optimum operating conditions. From the previous experiments dealing with the optimization of the NO detector, it seemed that the crucial parameters

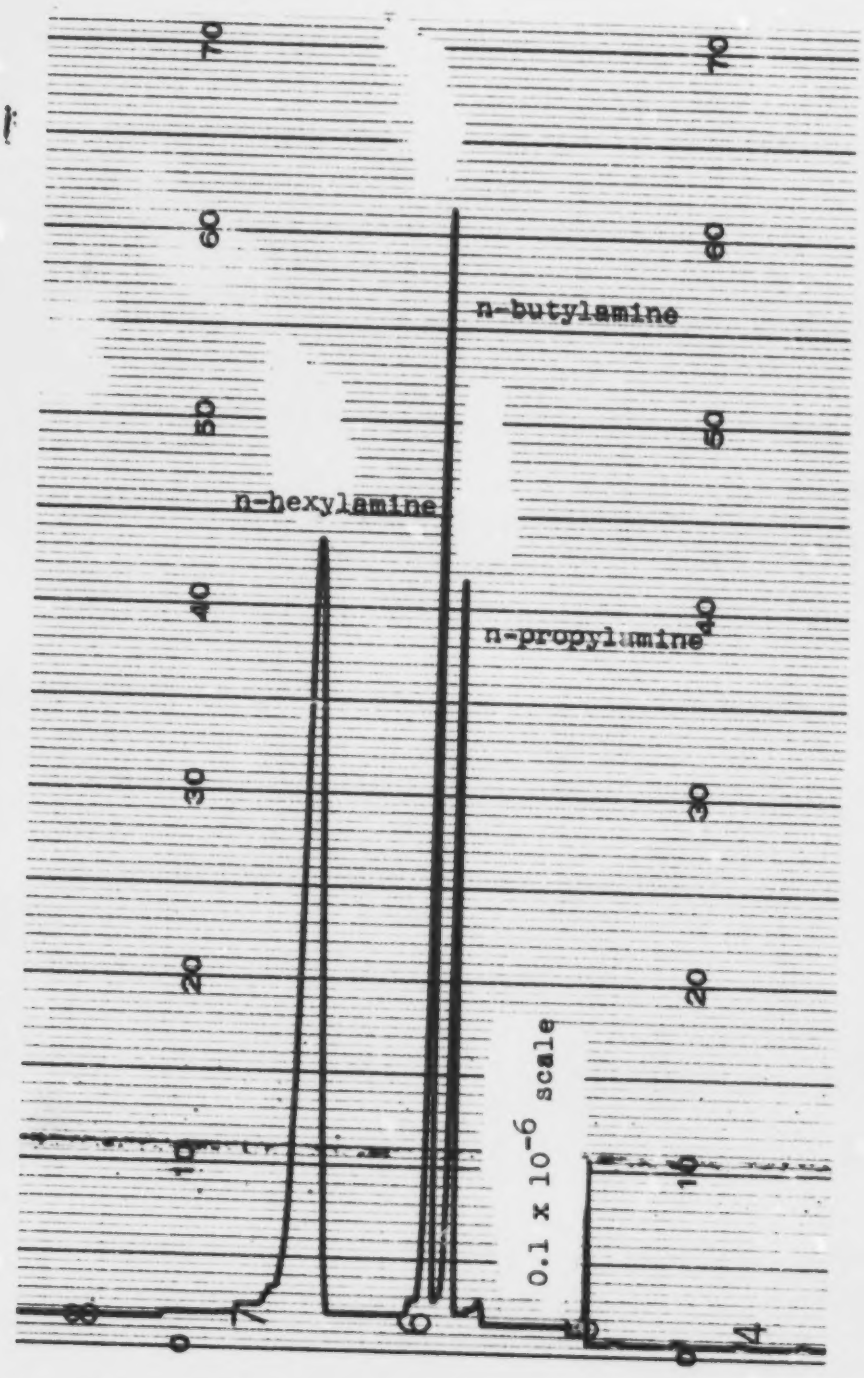

Figure 2. A chromatogram of a 1-µl sample of a mixture of n-propyl amine (14.7%), n-butyl amine (21.4%), and n-hexyl amine (63.9%) diluted by 1% by volume in benzene. The sample was run on a Chromsorb 103 column with column oven at 220°C, ozone flow to the detector of 30 cc/min, furnace at 795°C, and oxygen flow to the furnace of 2 cc/min. 70% of full scale is shown.

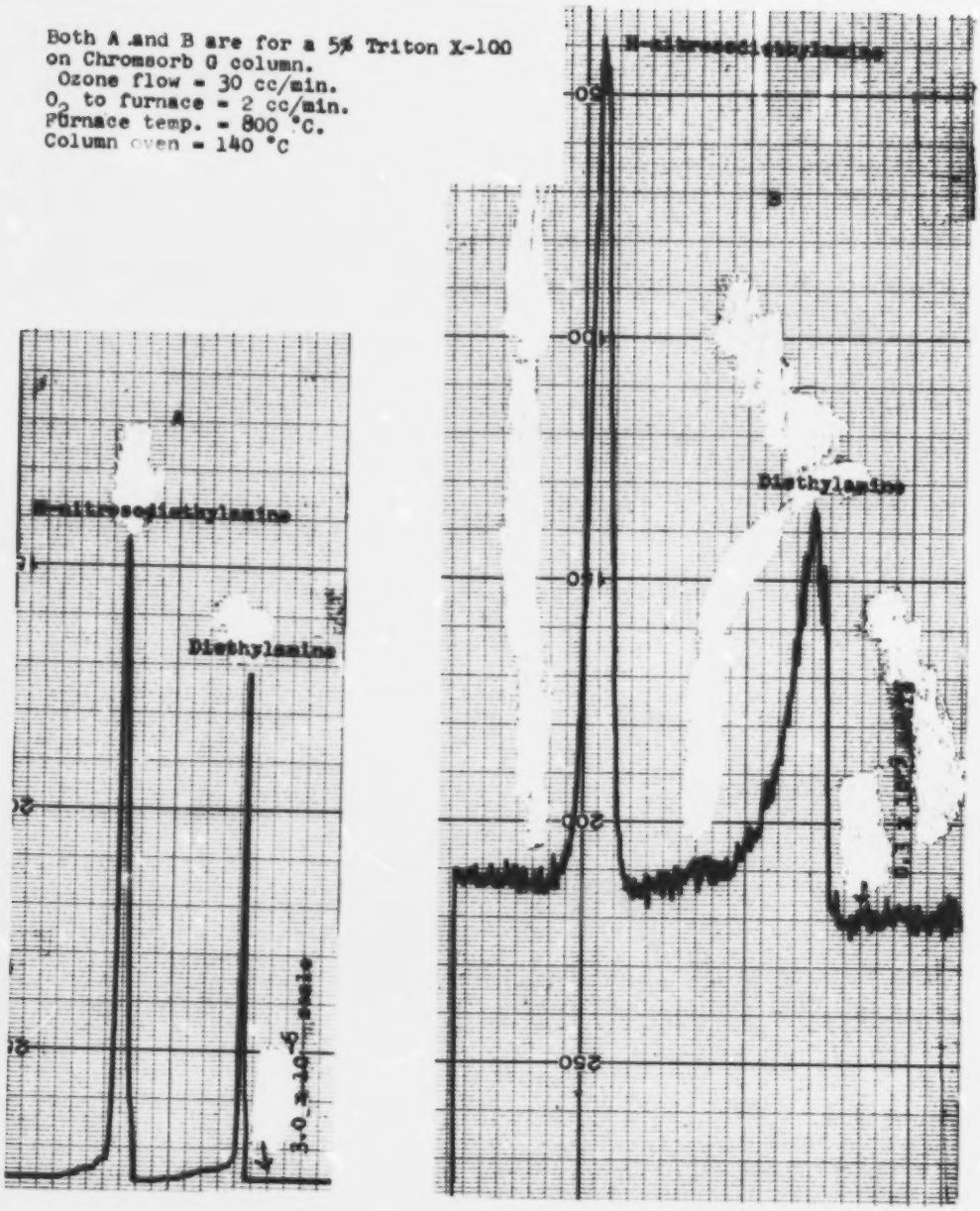

Figure 3

A. A chromatogram of 1 µl of a mixture of diethyl amine (8.9%), N-nitroso-diethyl amine (9.2%), and benzene (81.9%) by volume. 64% of full scale is shown. B. A chromatogram for 1 cc of a gas sample of the mixture in 3A after 250 min in the dilution bulb. The mixture in 3A was injected into the bulb to initially form 100 ppm of each component in the bulb. 90% of full scale is shown and both chromatograms have the same zero on the recorder.

would be 1) rate of ozone flow into the reactor of the NO detector, 2) rate of O_2 flow into the furnace and hence into the reactor, 3) furnace temperature, and 4) rate of sample flow into the reactor as controlled by the needle valve and measured by the Bourdon gauge.

Experiments showed that the first three were important parameters, but the 4th was unimportant, as long as the pressure in the furnace was atmospheric or less. If the needle valve was turned down until the pressure built up outside the reactor inlet, the signal dropped. The amount of vacuum was not critical, however, so the needle valve was left wide open for all of the experiments reported here and the vacuum varied from 17-22 inches of Hg.

The effects of the other three parameters has been indicated by presenting just a few of the data in Table I. All of these results are for injection of 1 µl of 1% diethylamine in benzene on a 5% polyetheylene imine on Chromsorb G. column. By comparing runs, 1,2,3, and 4, one can see that the O_2 flow into the furnace could have a large effect on signal. A minimum amount was required to efficiently oxidize the amine, but further flow raised the pressure in the reactor without increasing the NO flow. Since the NO detector signal varies directly with NO flow/pressure (2), the signal drops with increased O_2 flow. By comparing runs 4,5, and 6, one can see that the signal was completely insensitive to furnace temperature between 600 and 930°C. However, this might not hold true for larger or more thermally stable molecules, so the furnace has been kept at about 800°C or higher for all of the experiments reported on here. Finally, by comparing runs 7,8, and 9, one can

TABLE I. The Effect of Operating Parametric on the Detector Response to One µl Sample of One Percent (by Volume) Ditheylamine in Benzene

Run	Temp. °C	O_2 flow rate cc/min	O_3 flow rate[a] cc/min	Peak Area[b] (1 x 10^{-6} seale)
1[c]	807	2.0	35	20,112
2	807	∿0	35	6,087
3	807	7.0	35	13,650
4	807	5.0	35	17,361
5	931	5.0	35	17,504
6	600	5.0	35	17,180
7	745	5.0	85	15,258
8	745	5.0	8	16,280
9	807	2.0	35	18,965

a. Rate of flow of $O_3 + O_2$ from the ozonizer into the reactor.

b. Results from the integrator for samples run at 5% polyethylene imine on Chromosorb G.

c. Data taken five days apart without calibration.

see that the signal was somewhat sensitive to ozone flow, more precisely oxygen flow rate, through the ozonizer into the reactor. The detector was less sensitive to this parameter and a change of a factor of two only produced only a change of ± 25% in detector signal.

At the end of these experiments, it was determined that the optimum operating conditions for the detector for diethylamine were those shown in runs 1) and 9) in Table I, and they have been used for all of the other data reported here.

At this point there was some concern as to the stability and reproducibility of the detector. Experiments showed that on any given day, samples could be reproducibly detected to better than ± 2% and the limiting factor seemed tobe reproducibility of sample injection with the 10 µl syringe. On a day-to-day basis, however, the stability and reproducibility of the detector is still open to question. The initial results, shown in Table I, show about a 5% change over a five day period for diethamine, and this did not seem important at the time. However, the results shown in Table II over a longer time period show that the detector sensitivity has changed characteristically for both diethyl amine and N-nitrosodiethylamine over an interval of several months.

This change in detector signal was discovered in conjunction with experiments with smaller sample when it was noted that the response ratio of N-nitrosodiethylamine to diethylamine had changed. Originally we had been quite please that the nitrosoamine response

Table II. Detector Response for 1 µl sample of 1% Diethylamine and 1% N-Nitrosodielhylamine in Benzene. Peak Areas (1 x 10^{-6} scale)

Date	Column	Diethylamine	N-Nitrosodiethylamine
Dec, 1973	Polyethylene imine	18,965	36,346
March, 1974	Triton X-100	23,907	85,439
May, 1974	Polyethylene imine	26,047	118,302
May, 1974	Triton X-100	85[a]	324[a]

a. Integrator range used for earlier data was not working, so a different range was used. The relationship between the two is unknown.

(2 N atom per molecule) had been about twice the amine response (1 N atom per molecule), and were dismayed to discover that this ratio had changed. We satified ourselves that the absolute sensitivity had increased, and since this change did not effect more important experiments, we have not had time to experiment to find out why the sensitivity changed.

It could be the conversion furnace, the interaction and loss of the sample on the column walls of the G. C., or the integrator is the source of the change. Recently, either because of experiments where large amounts of UOP-55 were continuously injected into the G. C. or because of age, the conversion furnace has stopped functioning. Therefore, we plan to build a new one and to systematically measure sensitivity or a function of time, column material, and intergratior, which has also developed problems. In particular we want to establish absolute conversion percentages by calibrating the detector with a calibration gas of NO in N_2.

Once it had been established that the NO detector was indeed a N specific G. C. detector, the first task was to establish its limit of detectibility for diethylamine and N-nitrosodiethylamine. This turned out to be a harder task than anticipated.

The first approach was to pump out used 12 liter freon tanks and fill them with enough sample and nitrogen to have a tank of 100 ppm each of diethylamine and N-nitrosdiethylamine at three atmospheres pressure. The intent was to pass this calibration mixture through a flow meter and mix it with varying known flows nitrogen to produce known concentration of the two samples in the final mixture, which would then be injected into the G. C. However,

both compounds showed great affinity for the walls of the can, and even if they were used right after filling, only trace amounts of the sample could be found.

The second approach was to construct a 5.45 liter exponential dilution bulb with a magnetically driven vane stirrer inside the bulb for rapid mixing. By establishing a constant and measured flow of nitrogen through the bulb and then injecting enough diethylamine and N-nitrodiethylamine into the bulb to produce 100 ppm concentration at time zero, one could then take samples from the bulb as a function of time and get a decreasing concentration of the two compounds. A plot of log (response) versus time could be extrapolated to time zero where concentration was known and used to establish the concentration of the limiting response of the detector after a period of constant dilution.

This approach worked better,but not as well as we had hoped. The problem is the loss of the amine compounds on the walls of the vessel and gas handling system. It turns out that amines are very difficult to work with at the nanogram or ppm level. Indded we had noticed this problem in trying to calibrate the detector with dilute benzene solution of diethylamine and observed loss of sample on the walls of the flask and subsequent irreproducibility for 0.1% (1 microgram in one microliter of solution and 0.01% (100 nanograms in one microliter of solution) solution. With gas phase samples in the dilution bulb, initial results indicated that most of the sample disappeared onto the walls of the bulb and even mildly heating the bulb would not bring them off. Attempts to dry the walls to coat the walls with a silicone solution (Desicote), and to pass NH_3 through the bulb to deactivate the walls did not stop the loss of sample in the bulb.

What eventually produced the best results was to leave samples of th amines in the vessel to saturate the walls and then pass N_2 through the bulb until the background was negligible and then do the dilution experiment. The best results obtained are shown in Figure 4, and they are not completely satisfactory. The initial concentration of the two compounds should have been about 100 ppm, but the G. C. response was similar to the response obtained for 54.8 ppm NO in N_2. The dilution rate of the bulb was fixed so the half-life of sample in the bulb was 55 minutes. On this basis the results for N-nitrosodiethyl amine appears in good agreement, but that for diethylamine is clearly out of line. We hope to obtain better results in subsequent experiments.

We can use the results in Figure 4 to establish an upper limit for the detectibility of N-nitrosodiethylamine with our detector. Figure 2 B shows the chromotogram for the last point ploted in Figure 4 at 250 minutes. Where the initial detector response for the 100 ppm (or less) sample has been reduced by a factor of 20 (1.3 log units). This would indicate that the response in Figure 2B is for a sample that is now 5 ppm (or less) in the nitrosamine, and the peak in Figure 2B could certainly be reduced by a factor of 10 more and be readily detected. Thus a sample of the nitrosoamine of 1 to 0.5 ppm in a 1 cc gas sample (1 to 0.5 nanograms of sample) or less should be detectible with this detector.

Clearly the current calibration system is not satisfactory, and recent conversations with Dr. D. F. S. Natusch of the University of Illinois has put us onto a better approach for these calibrations.

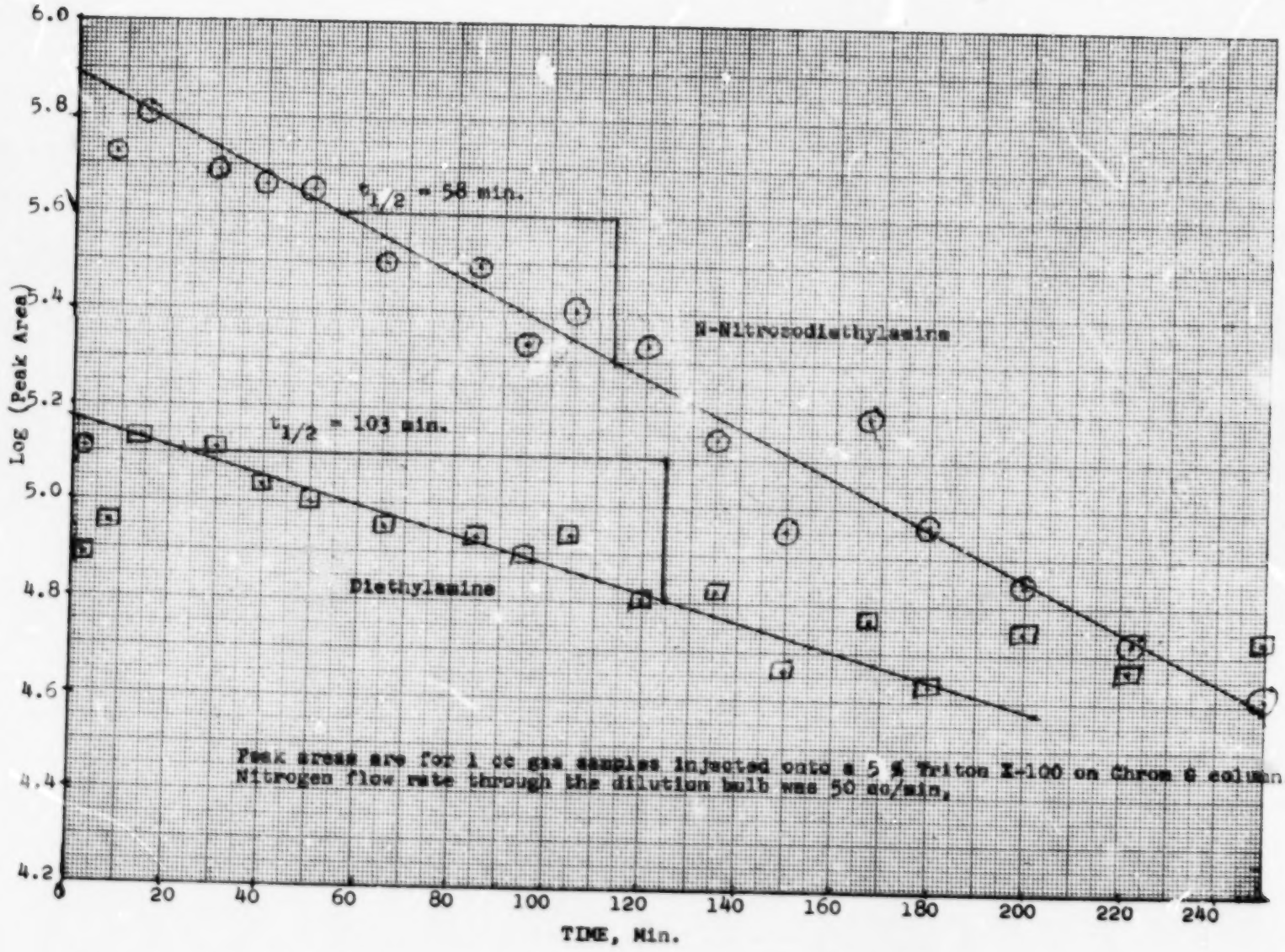

Figure 4. Plot of log (peak area) vs. time for an initial concentration of 100 ppm diethyl amine and 100 ppm N-nitroso-diethyl amine in the 5.45-liter exponential dilution bulb.

He had encountered similar problems in working with sulfur compounds, and has suggested an approach using a diffusion cell for continously adding small amounts of the test gases to a flow system from a detachable sample tube that can be weighed. This system, much like a permeation tube can be run continously until the walls are saturated, and it is similar to several described in Nelson (3) and references therein, and need not be discussed further here. We are currently building a similar piece of apparatus for repeating these sensitivity studies for several compounds with our detector and with the flare ionization detector for comparison.

We are in position, however, to make some judgment as to the quality of this detector as a N specific NO detector.

For high concentration sample of 0.1% or better, the detector clearly does a beautiful job. In Table III, the results of analysis of two amine mixtures supplied with the Polyscience Qual-kits of amines is shown, and agreement, without any calibration of the detector is quite satisfying.

The detector also was used to make a rough measurement of the total N in gasoline. 1 ml samples of gasoline were injected into a Triton X-100 column, and the results are shown in Table IV. Since gasoline fuel nitrogen has been determined

Table III. Detector Response for two Amine Mixtures.

A. Secondary Amines

Compound	% Given	% Found	Column
Diethylamine	15.2	15.5	Polyethyleneimine
Di-n-propylamine	20.6	21.5	"
Di-n-butylamine	26.1	25.7	"
Cyclohexylamine	38.2	37.3	"
B. Primary Amines[a]			
n-Propylamine	21.6[a]	16.6	Polyethyleneimine
n-Butylamine	24.8[a]	23.2	"
n-Hexylamine	53.6[a]	60.2	"
n-Propylamine	21.6[a]	14.7	Chromsorb 103[b]
n-Butylamine	24.8[a]	21.4	
n-Hexylamine	53.6[a]	63.9	

[a]The bottle containing the primary amine had leaked, and continued to leak. These two analyses were run several weeks apart and the sample continued to lose the lighter amine relative the others.

[b]This data is shown in Figure 1.

TABLE IV Detector Response for 1 ml samples of gasoline

Sample	Peak Area (10 X 10^{-9} Scale)	Column
gasoline[a]	31,775[b]	Triton X-100
54.8 ppm NO in N_2	39,794	Triton X-100
54.8 ppm NO in N_2	31,163	Polyethyleneimine

[a]The gasoline was a sample taken from a can that had been stored for 15-20 months.

[b]Average of three determinations

to be from 5-30 ppm by micro-kjeldahl techniques, the agreement with the 54.8 calibration gas sample is encouraging. In fact, with proper calibration or addition of an internal standard, this detector shows real promise as a means of rapid and accurate analysis of total fuel nitrogen or other nitrogen analysis at the nanogram level.

Finally we can make some comparison of over N specific detector with other N specific G. C. detectors. A recent review of element selective detectors for gas chromatography (4) puts the sensitivity of the Coulson conductivity detector (such as the tracer electrolytic conductivity detector) at a limit of 100 picograms of N which would require at least 0.5 to 1.0 nanograms of parent sample. This is the upper level of sensitivity we have estimated for our detector for N-nitrosodiethylamine. However, we have almost two orders of magnitude of sensitivity left on our NO detector, which is currently hidden by

background from the column and conversion furnace. As yet we have not done anything to reduce this background, but our detector does have the potential to be two orders of magnitude better than any other currently available. One of our future projects is to increase this sensitivity in conjunction with better calibration techniques discussed above.

Flat Flame Burner Studies

In spite of the difficulties in clearly establishing the sensitivity limits of our detector, we felt that we had established the fact that we could see at least 1 ppm quantities of nitrogen containing molecules, and thus we moved on to preliminary experiments with the flat flame burner.

The burner was borrowed from Dr. W. Mirsky of the Automotive Engineering Department of the University of Michigan, where it had been constructed and used by Dr. A. Gad El-Mawler in his Ph.D. research (5). The burner itself was constructed of a 2 in. diameter, 6 in. long copper tube having at the upper and lower ends 1/4 in. thick porous discs of sintered brass, 90% copper and 10% tin. The space between these discs was filled with 3 mm diameter glass beads to provide mixing of the propane fuel and air, and to produce an even flow to the top of the burner. The burner was housed in a thick-walled, cylindrical iron-chamber provided with four 3-in diameter viewing and access parts. The burner could be raised or lowered

vertically without rotation through a distance of about 1/2 in by a screw mechanism at the bottom of the chamber. The propane from a liquid propane gas cylinder and air from a cylinder of dry compressed air were put into the burner by a tee at the bottom of the burner. The burner was lit by sending a spark through a copper wire to the burner with a tesla coil.

A reproducible flame was maintained by adjusting the regulator made valve and second stage pressure until a slightly fuel lean flame of adequate size was established and then fixing the valves and the regulator pressure screws at these positions. The flame was then turned on and off by opening and closing the valves between the tank and the first stage of the regulator. The flow of air was measured to be about 15 liters/min with a wet test meter and the flow of propane was measured to be about 0.6 liter/min.

The sample of additive was added to the flame by preparing an appropriate solution of the additive in benzene (in the neighborhood of 10% to minimize the injection of benzene) and injecting it through an 8 mm quartz tube, drawn to a fine tip, at a constant rate with a continuous infusion -- withdrawal syringe pump (Harvard Apparatus Model 901). The rate of infusion and additive concentration were chosen to provide a certain ppm concentration in the 15.6 l/min of air/propane passing through the burner.

Currently the additive is injected directly into the

burner flame. There is an opening into the copper tube of the burner body where samples could be injected directly into the unburned gases before they reach the top plate. The temperature here was measured to be only 65°C, and the UOP-55 would not be readily vaporized at this temperature. For future work, we plan to put heating tape around the burner so all additions to the flame can be made into the unburned gas.

Samples are withdrawn from the flame by another 8 mm quartz probe drawn down to a tip which is mounted vertically over the flame and can be moved to several positions in the flame. A 30 cc syringe is attached to the probe at a tee with a rubber septum at the third position. Samples are drawn into the syringe and a sample is obtained with a 2 cc gas syringe through the septum for direct injection into the gas chromatograph.

At this point in time, all our results with the burner are negative as far as finding any combustion products for the UOP-55 additive. We have shown that with 1000 and 100 ppm concentration of diethylamine, we can see the amine in the unburnt gases, but after the flame is lit, all peaks disappear from the G. C. Turning the flame off by turning off the propane does not cause the diethylamine to reappear as long as the burner and probe remain hot. With similar samples of the disalycylidene propane diamine, nothing was detected either before or after the flame was turned on. Since we do not have a G. C. column that will pass this compound at low concentrations, this result was not surprising.

These burner experiments are far from completed. We have just begun to think about trying different probe positions or sampling techniques and different flame tempertures (the burner has cooling coils just under the top plate). Earlier work with the burner clearly found unburned hydrocarbons in the propane flame (5), and we have yet to find the right conditions to find amine fragments from simple amines. Once these are established, we can then have more meaningful attempts to find combustion fragments for the fuel additive.

Conclusions and Future Plans

Because this research is not yet completed this report included some discussion of incomplete experiments and negative results. However, we are planning to continue this research for more than another year, in which time we will try some of the new, and hopefully better, techniques discussed above. We have developed a new and promising N specific detector for gas chromatography that is at least as sensitive to N-nitrosodiethylamine as any similar N specific detector. We hope to improve and establish the sensitivity and reliability of this detector for a variety of amine compounds including the fuel additive. We have begun a series of flat flame burner studies that need further experimental adjustments before they can be adequately used to look for fuel additive combustion products. At this point we remain optimistic that we can deal with these problems before fall and may be able to move on to the engine studies portion of this project.

Some particular steps to be taken are:

a) Use of glass or teflon columns for fuel additive.

b) Upgrading and writing a complete report on the N-selective GC method.

c) Provision to E.P.A. of a converter furnace and specifications for use with their chemiluminescent detector.

d) Future flame studies as described earlier, leading to engine studies if successful.

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OPTIMIZATION OF THE OPERATING PARAMETERS OF CHEMILUMINESCENT NO DETECTORS

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Abstract

The parameters that effect the sensitivity of a typical chemiluminescent NO detector have been investigated. Using a 54.8 ppm in N_2 sample and an $NO:O_3$ flow ratio of 2:1, the detector signal was measured as a function of reactor pressure at several different pumping speeds in different reactors. The results are consistent with an analysis of the kinetic limitations on the chemiluminescent intensity, which shows that Detector Signal=(Reactor Gas Flow/Reactor Pressure)(G)(1-exp($-\tau_{react}/\tau_{NO}$)) where G is the geometry of photon collection of the reactor and $\exp(-\tau_{react}/\tau_{NO})$ is the fraction of NO molecules whose residence lifetime in the reactor (τ_{react}) is short compared their reactive lifetime with O_3 (τ_{NO}). From this equation, and results using different reactor designs and different photomultipliers, it is shown that the relevant parameters for optimizing the detector are pumping speed, reactor size, O_3 flux, reactor design, and choice of photomultiplier. The choice of these parameters is discussed and they are somewhat different for an atmospheric NO monitor from those for a laboratory detector for limited samples.

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The use of chemiluminescent nitric oxide detectors has grown rapidly in the past few years, particularly as air pollution monitoring instruments for atmospheric concentrations of NO_x. A recent review of chemiluminescent detectors used in the measurement of air pollutants (1) lists nine different manufacturers of commercial NO_x detectors even though the feasibility of such detectors was only established by Fontijn et al (2) in 1970, and the prototype for a number of these commercial instruments was developed in 1972 (3). Besides their application as monitors for atmospheric NO, these detectors have been used as laboratory analytical instruments for measuring NO as a product or reactant in standard kinetic or photochemical experiments (4).

In spite of the growth and rapid development of commercial instruments, there has been little systematic study of the physical and kinetic parameters that determine the optimum sensitivity of the NO detector. The basic design and the components of the detector have been established, but there remains a wide latitude of choice of the operating capabilities of each component. These choices must also be compatible with the basic kinetic limitations of the chemiluminescent $NO-O_3$ reaction. Furthermore, operating conditions for use in atmospheric gas monitoring where the supply of sample is virtually unlimited are not necessarily ideal for use in the laboratory to detect NO in a limited amount of sample.

In this work we have systematically studied the operating parameters and reactor design that effect the intensity of the chemiluminescence that reaches the photomultiplier tube of the detector.

This intensity was found to be a function of pumping speed and the flow parameters of NO and O_3 into the reactor in a way that is quite consistent with the proposed kinetics and mechanism of the reaction. The intensity is also a function of physical parameters, particularly reactor design, that facilitate getting the light to the photocathode of the photomultiplier. Finally we made a few experiments with a different photomultiplier to demonstrate how important the choice of photomultiplier is to the ultimate sensitivity of the detector.

Experimental

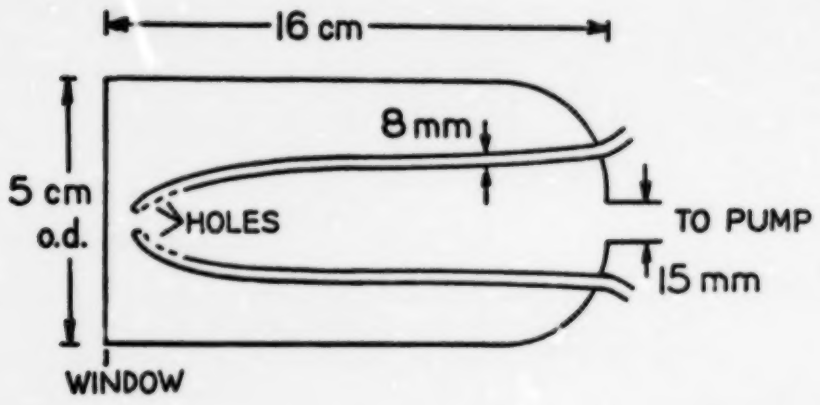
The schematic design of the NO/O_3 chemiluminescent detector used in these experiments is identical to those published earlier (1, 3), and is similar to those of commercial instruments. The photomultiplier used in most of the experiments was an RCA 8852 with an ERMA III response that extended its range to 900 nm. It was dry ice oled and nitrogen gas from a tank was slowly passed through a small space between the reactor window and the photomultiplier window to prevent frost formation. A Kodak Wratten gelatin filter was used to remove any emission below 600 nm. A few experiments were made using an Amperex 150 CVP photomultiplier with an S-1 response and nitrogen gas vaporized from a Dewar of liquid nitrogen was used for cooling. The power supply for the photomultiplier was a Heath EU-42A variable high voltage power supply with a maximum output of 1500 volts. The photocurrent was measured with a Keithly 414S picoammeter whose output was displayed on a Honeywell 10 mv strip-chart recorder.

A Cenco Hyvac 14 pump was used to maintain the flow of NO and O_3 through the reactor, and a bellows valve was installed in

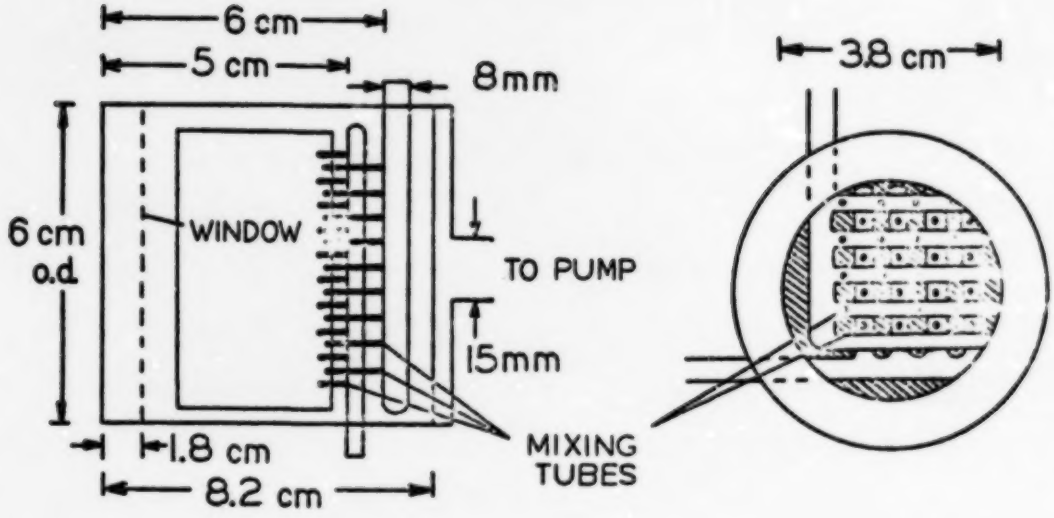
front of the pump in order to vary the pumping speed. The flows of NO and O_3 into the reactor were controlled with teflon needle valves and the flow rates were measured with Gilmont No. 11 or No. 12 flow meters. The flow meters were calibrated with a wet test meter or by displacing water from a volumetric flask.

For these experiments, the instrument was used as an NO detector with a tank of Linde 54.8 ppm NO in N_2 as the NO source for all of the experiments. Oxygen was passed through an ozonizer operated at 9000 volts. The pressure in the reactor was measured with either a mercury or oil manometer using a cathetometer to read the manometer levels to .05 mm.

Four different reactors were used in these experiments in order to test design features that might increase the sensitivity of the detector. The design and dimensions of the two reactors used for most of the experiments are shown in Figure 1. The smallest reactor, referred to hereafter as the "brass reactor", effective volume about 36 cc, was designed to facilitate rapid and effective mixing of NO and O_3 with the gases emerging from small jets interleaved with one another and surrounded by a glass cylinder to guide the reactants toward the front window before being pumped down the sides and out the back. The other reactor, referred to hereafter as the "glass reactor", volume about 300 cc, was designed to mix the reactant gases as close to the window in front of the photomultiplier tube as possible. The other two reactors were also made of Pyrex glass, and were similar to the glass reactor in Figure 1. One was identical except that the outlet to the pump was two 10 mm tubes exiting at the front of



GLASS REACTOR



SIDE VIEW

FRONT VIEW

BRASS REACTOR

Figure 1. Cross-sectional designs of the two main reactors used in the NO detector. Both the window and the internal glass cylinder of the brass reactor had a diameter of 3.8 cm, which limited the effective reaction volume open to the photomultiplier.

the reactor near the window. The other was larger, about 20 cm long and about 400 cc volume, but the gas inlets had only one hole in the end and they pointed straight forward with a separation approximately four times that of the glass reactor. This reactor provided the poorest mixing of NO and O_3.

With both the glass reactor and the brass reactor, at the highest pumping speed, the maximum photocurrent was obtained with an NO:O_3 flow ration of 2:1 (where O_3 refers to the O_2/O_3 mixture from the ozonizer). This flow ratio was used for all of the experiments. The pumping speed was varied by a factor of ten, so that the total gas flow in the reactor as measured by the calibrated flowmeters and corrected for the reactor pressure, varied from around 170,000 ml/min to 17,000 ml/min. Thus the residence time of the gases in the reactor ranged from about 0.11 sec to 1.1 sec for the glass reactor and from about 0.012 sec to 0.12 sec for the brass reactor. In almost all of these experiments the high voltage power supply for the photomultiplier was set at 1140 volts. A few measurements were made at 1500 volts. Usually the photomultiplier was cooled with dry ice, but cooling was not critical since the cooled and uncooled signals were identical and only the dark current was reduced.

Results

The experiments were designed to measure the intensity, I, of the chemiluminescence for the 54.3 ppm sample as a function of reactor pressure. This pressure was varied by changing the total flow of reactants through the reactor. The results are shown in Figures 2 and 3 for the glass and brass reactors, each at three different pumping speeds. The pumping speeds were determined from

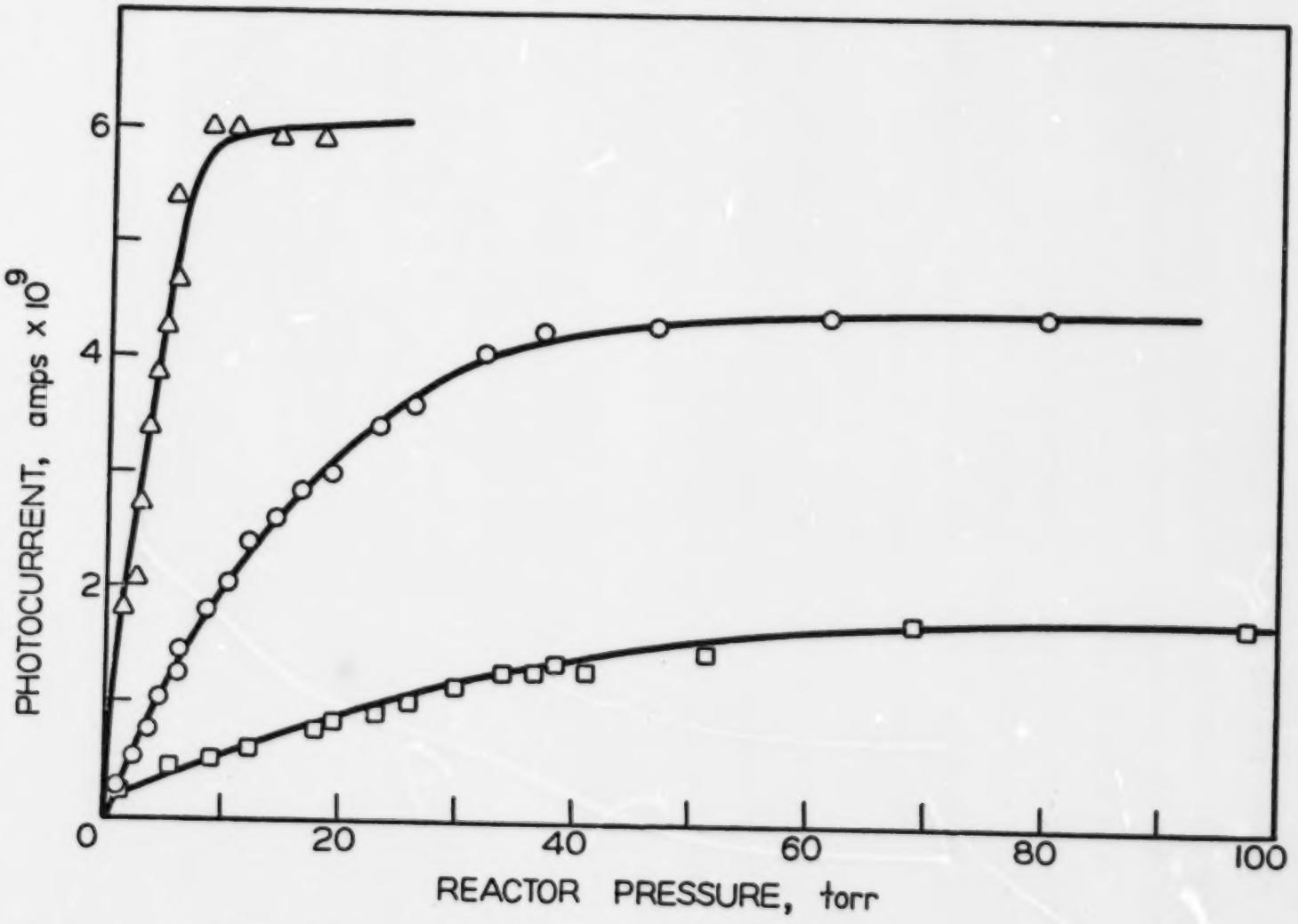


Figure 2. NO detector signal as a function of reactor pressure at three different pumping speeds for the glass reactor. Δ = data at 136 l/min, O = data at 63 l/min, and □ = data at 30.5 l/min.

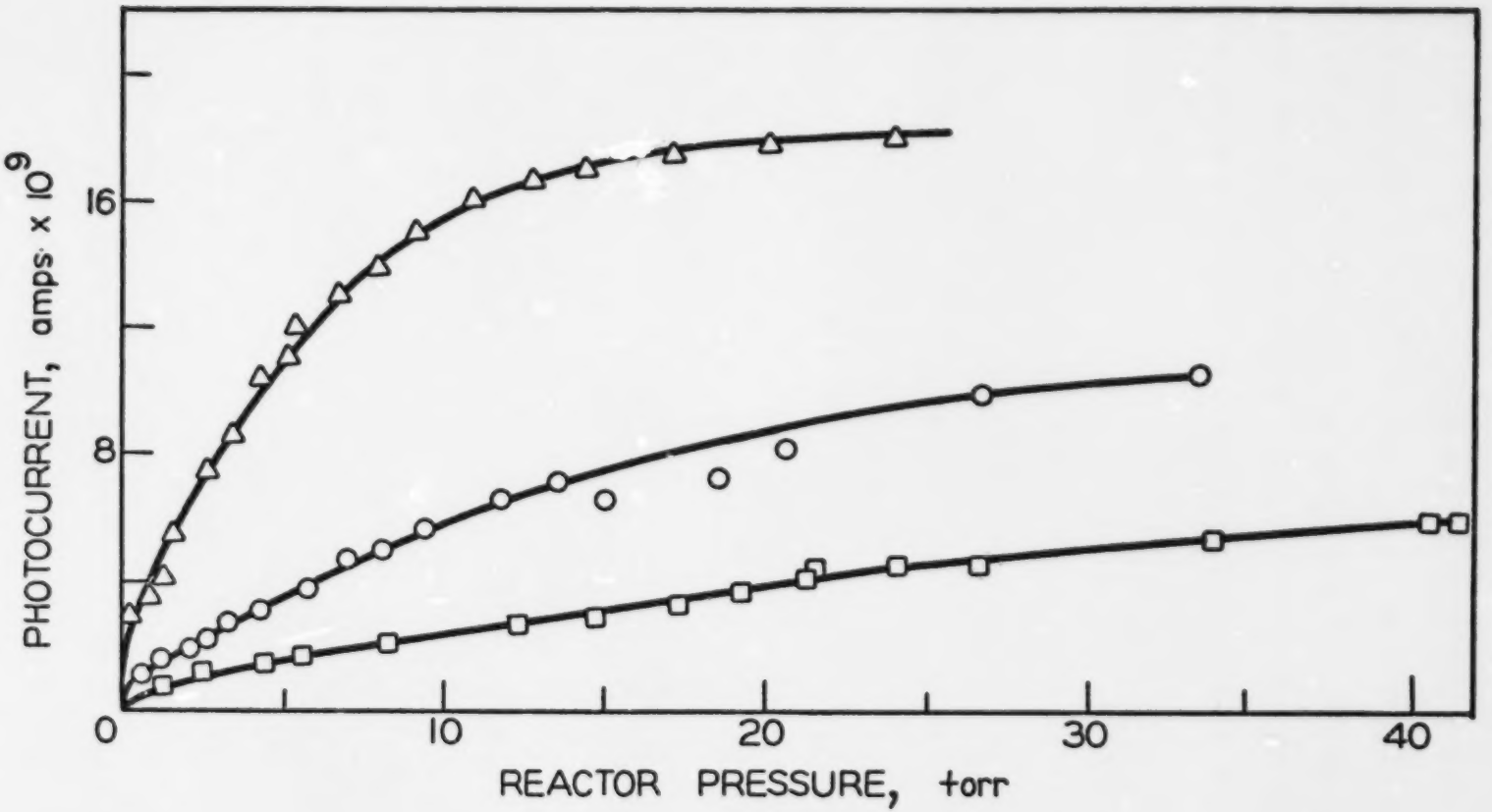


Figure 3. NO detector signal as a function of reactor pressure at three different pumping speeds for the brass reactor. Δ = data at 136 l/min, O = data at 40.5 l/min, and □ = data at 16 l/min. The last □ at the 16 l/min pumping speed represents experimental points at 71 and 108 torr with that ordinate value.

the total flow and the pressure in the reactor, and they are plotted in Figure 4 as a function of pressure.

The effect of reactor designs on the sensitivity of the detector is shown in Table I along with data for the dark current and noise of the photomultiplier. Table I also shows the change in signal and dark current achieved by an S-1 response photomultiplier.

Discussion

The main parameters that can effect the signal intensity of the detector can be understood through the kinetics and mechanism of the NO-O_3 reaction, and the relationship of the residence lifetime of the reactants in the reactor to their kinetic lifetime. The mechanism of the reaction between NO and O_3 has been previously established (5, 6)

$$NO + O_3 \longrightarrow NO_2^* + O_2 \qquad (1)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (2)$$

$$NO_2^* \longrightarrow NO_2 + h\nu \qquad (3)$$

$$NO_2^* + M \longrightarrow NO_2 + M \qquad (4)$$

where NO_2^* is an excited electronic state which emits radiation between 600 and 3000 nm with a maximum at 1200 nm. The rate constants for (1) and (2) were measured to be $k_1 = 1.1 \pm 0.6 \times 10^{-15}$ cm^3 $molecules^{-1}sec^{-1}$ and $k_2 = 1.4 \pm 0.6 \times 10^{-14}$ cm^3 $molecule^{-1}sec^{-1}$.

If the only important reactions were (1) and (3), then all of the NO molecules entering the reactor would emit photons, thus

$$I_{tot} = f_{NO} \qquad (5)$$

where I is the intensity of the signal in photons sec^{-1} and f_{NO} is the mass flow of NO into the reactor in molecules $sec.^{-1}$ In fact,

Table I. The Effect of Reactor Design and Photomultiplier Voltage on the Signal, Dark Current, and Noise of a Chemiluminescent NO Detector.

RCA 8852 ERMA III Response

Reactor	1140 volts		1500 volts	
	Signal, amps	Dark Current & Noise, amps	Signal, amps	Dark Current & Noise, amps
1. brass (36cc) (see Fig. 1)	6.0×10^{-9}	$2^{\pm} \times 10^{-12}$	6.2×10^{-8}	$4 \pm 4 \times 10^{-11}$
2. glass (300cc) (see Fig. 1)	18.0×10^{-9}	n.m.	3.2×10^{-7}	n.m.
3. glass (300cc) (same as 2 with front pumping)	3.2×10^{-9}	n.m.	n.m.	n.m.
4. glass (400cc) (same as 2 with poor gas mixing)	6.5×10^{-9}	$8 \pm 4 \times 10^{-13}$	1.4×10^{-7}	$3 \pm 2 \times 10^{-11}$
5. glass (300cc) (same as 2 with reflective coating)	60.0×10^{-9}	$2 \pm 1 \times 10^{-12}$	n.m.	n.m.
Amperex 150CVP, S-1 Response				
6. brass (same as above)	70×10^{-9}	$9 \pm 0.4 \times 10^{-11}$*	n.m.	n.m.

* The dark current is very dependent on the cooling efficiency and this represents the lowest value found over a four day period. On other days it was as much as 20 times higher.

the above kinetics impose three constraints on equation (5). 1) Only a fraction, $k_1/(k_1 + k_2) = .073$, of NO + O_3 encounters leads to excited NO_2^*. 2) Quenching of NO_2^* allows only a fraction, $k_3/(k_3 + k_4[M]) = 8.3 \times 10^{-3}$ at 1 torr, of the possible photons to be emitted. 3) The rate of reaction of NO + O_3 is relatively slow which allows a fraction of the entering molecules, $\exp(-\tau_{react}/\tau_{NO})$, to leave the reactor untouched, or allows only a fraction, $(1-\exp(-\tau_{NO}/\tau_{react}))$, of the entering NO molecules to react inside the reactor. Here τ_{NO}, the reactive lifetime of NO, is the inverse of the pseudo-first order rate constant for the reaction of NO in the presence of excess O_3,

$$\tau_{NO} = 1/((k_1 + k_2)[O_3]), \text{ sec} \qquad (6)$$

and τ_{react}, the residence lifetime of the reactants in the reactor, is determined by reactor size and the flow rate in the reactor,

$$\tau_{react} = (A)(d)(P)/F, \text{ sec} \qquad (7)$$

where A is the cross sectional area of the reactor in cm^2, d is the reactor length in cm. P is the reactor pressure in molecules cm^{-3}, and F is the total flow in molecules $sec.^{-1}$ The above expression for the fraction of unreacted NO molecules derives from the pseudo-first order kinetics of equation (1) and (2). The fraction of unreacted NO molecules present at the end of the reaction is

$$\frac{[NO]_{t=\tau_{react}}}{[NO]_{t=0}} = \exp(-(k_1 + k_2)[O_3]t) = \exp(-\tau_{react}/\tau_{NO}) \qquad (8)$$

where $t = \tau_{react}$. Therefore, with the above three constraints on equation (5), the light emitted from the reaction zone becomes

$$I_{tot} = (f_{NO})\left(\frac{k_1}{(k_1 + k_2)}\right)\left(\frac{k_3}{(k_3 + k_4[M])}\right)(1-\exp(-\tau_{react}/\tau_{NO})) \quad (9$$

photons per second.

In practice we cannot collect all of the photons emitted, so the signal from the photomultiplier is not I_{tot}, but has been attenuated by a further factor G which includes the geometry of photon collection and photomultiplier characteristics. Since $k_4[M] \rangle\rangle k_3$ and [M] is the pressure in molecules cm^{-3}, equation (9) can be written

$$\text{Signal} = \left(\frac{f_{NO}}{P}\right)(G)\left(\frac{k_1 k_3}{k_4(k_1 + k_2)}\right)(1-\exp(-\tau_{react}/\tau_{NO})) \qquad (10)$$

This is the signal measured by the picoammeter and has been plotted as a function of reactor pressure in Figures 2 and 3.

For the moment assume $\tau_{react} \rangle\rangle \tau_{NO}$, so that most of the NO molecules react inside the reactor, and we can neglect the exponential portion of equation (10). In this case, the signal is directly proportional to f_{NO}/P or F_{tot}/P since the NO flow was a fixed fraction (2/3) of the total flow. One can enhance the signal by increasing f_{NO}, decreasing P, or increasing f_{NO}/P. For NO detectors with a constant volume vacuum pump, f_{NO} and P are not independent of one another. If one doubles the flow of NO molecules into the reactor, one simultaneously doubles the pressure. One can only increase the signal by increasing f_{NO}/P. Since f_{NO}/P is in units of $cm^3\ sec^{-1}$, it is a measure of pumping speed and it can be increased by increasing the speed of the pump.

Figure 4 shows the different pumping speeds utilized in these experiments. Comparison of this data with the signal intensities

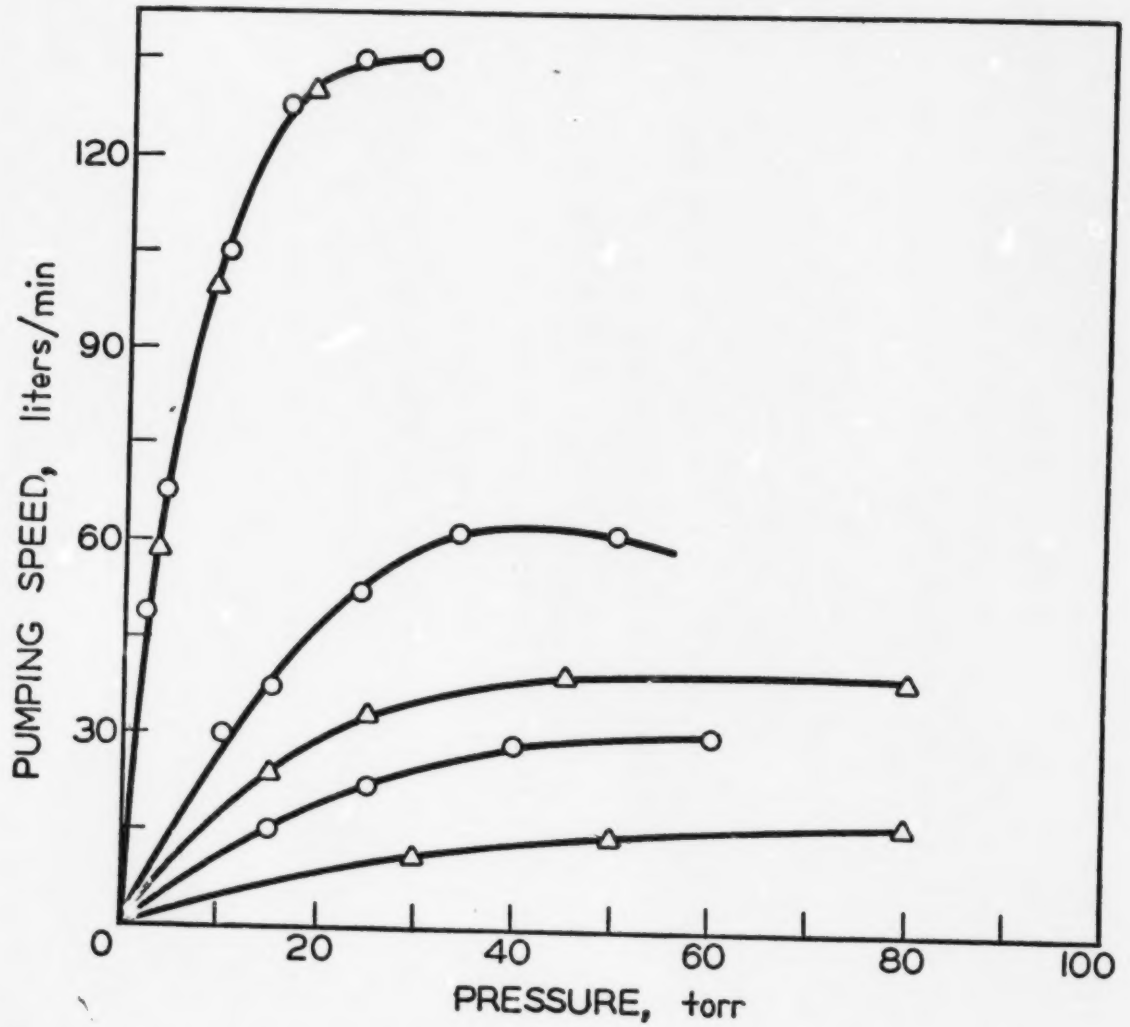


Figure 40. Pumping speed as a function of reactor pressure. O = data collected with the glass reactor and Δ = data collected with the brass reactor. Pumping speed can be coverted to F/P in units of cm^3 sec^{-1} $torr^{-1}$ by multiplying the numbers along the ordinate by 7.85.

in Figures 2 and 3 gives excellent qualitative agreement as predicted by the above analysis. Decreasing pumping speed does decrease the photomultiplier signal.

The fall-off in pumping speed at low pressures, which is matched by an identical fall-off in signal, deserves some comment. The speed pressure curve for the Cenco Hyvac 14 (140 l/min maximum pumping speed) indicates that the pumping speed should be almost constant in this pressure region, and such a fall-off should not occur until 10^{-3} torr. However, at low pressures, pumping speed is often limited by the "resistance" of smaller tubing in part of the pumping system (7), and here the tubing from the reactor to the pump, including the ozone-killer section, filled with wire, in front of the pump, causes the early onset of the fall-off in pumping speed at low pressures.

Quantitatively, on the basis of equation (10), one would expect a plot of signal vs pumping speed to be linear with a zero intercept and a slope that varies with G. the geometry of photon collection for a particular reactor. Such a plot, using the data from Figures 2 and 4 for the glass reactor, was indeed linear with a zero intercept. For the brass reactor, using the data in Figures 3 and 4 only the data for the lowest two pumping speeds falls on a straight line through the origin. As predicted, the slope of this line for the brass reactor was different from that of the glass reactor, but the signal for the highest pumping speed was 2.5 times lower than that predicted by this plot. Clearly a large fraction of the possible signal had been lost.

In order to understand the strong attenuation in the signal in the brass reactor at high pumping speeds, we must examine the $(1-\exp(-\tau_{react}/\tau_{NO}))$ term previously neglected in equation (10). If the residence lifetime of NO and O_3 in the reactor gets short, compared to the reactive lifetime of NO, as one might expect at high pumping speeds in a small reactor, then some fraction of the photons are emitted outside the reactor, and the signal is attenuated by the fact that only a fraction of NO molecules, $(1-\exp(-\tau_{react}/\tau_{NO})$ will actually emit light within sight of the photomultiplier. Thus, one cannot increase the sensitivity of an NO detector without limit by just increasing the pumping speed. One must consider the limitations of τ_{react} and τ_{NO} in optimizing the NO detector signal.

From Equation (7) one can see that τ_{react} is inversely proportional to F/P and thus is a constant for a given pumping speed except at low pressures where it increases as pumping speed falls off. In the experimental section it was noted that τ_{react} was 0.11 sec for the glass reactor and 0.012 sec for the brass reactor at the highest pumping speeds in the pressure region where F/P is constant.

Equation (6) gives the expression for τ_{NO}, which can be put in a more useful form by expressing $[O_3]$ as

$$[O_3] = (P)(\%O_3)fo_2/F \qquad (11)$$

where P is the reactor pressure in molecules/cm^3, $\%\ O_3$ is the mole percent of O_3 produced in the oxygen streaming through the ozonizer, and fo_2/F is the fraction of the total flow in the reactor that is $O_3 + O_2$. Substitution of equation (11) into equation (6) gives

$$\tau_{NO}=F/[(k_1+k_2)(P)(\%\ O_3)(fo_2)] \qquad (12)$$

Since $(k_1 + k_2)$ and F/P are constant, the important variable is the product of the oxygen flow in the reactor and the percentage of O_3 produced in the oxygen. This however is also constant rather than variable.

Using an ozonizer similar to the one we used in our NO detector, Jack Horvath at the Space Physics Research Laboratory at the University of Michigan measured the mole percent O_3 in O_2 as a function of fo_2 at several ozonizer voltages. He found that the mole % of O_3 decreased as the flow of oxygen through the ozonizer increased, and the ozonizer produced a constant flux of O_3 (8). At 9000 volts (the operational voltage of our ozonizer), the $(\%\ O_3)(fo_2)$ product was effectively constant at $1.25 \pm .05 cm^3/min$, over an O_2 flow range of 60 to 2160 cc/min as measured on the external flow meter. This covers all but the lowest flows of oxygen used in our experiments.

Thus τ_{NO} should be constant for a given pumping speed except at low pressures where it decreases as the pumping speed falls off. For the highest pumping speeds in the pressure region where F/P is constant in either the brass or glass reactor, τ_{NO} is 0.073 sec using the values of $(\%\ O_3)(fo_2)$ from the calibrated ozonizer:

Since both τ_{react} and τ_{NO} are constant when F/P is constant, their ratio is also constant:

$$\tau_{react}/\tau_{NO} = (Ad)(\%\ O_3)(fo_2)\ P^2/F^2 \qquad (13)$$

the NO detector signal, equation (10), will be optimized if τ_{react}/τ_{NO} is large so that $\exp(-\tau_{react}/\tau_{NO})$ is negligible. This fraction is negligible in these results except for the brass reactor at the

highest pumping speed where the signal is severly attenuated compared to the glass reactor. According to equations(10) and (13), this signal loss is due to the smaller volume of the brass reactor and the subsequent escape of unreacted NO from the reactor.

The easiest way to keep τ_{react}/τ_{NO} large in an NO detector is to make the reactor volume (Ad) large. This will help compensate for the fact that an increased pumping speed, F/P, which has been shown to directly enhance the signal, can also decrease the signal by lowering this ratio by a factor of $(P/F)^2$. One might further increase this ratio by increasing the efficiency of O_3 production which would increase the % O_3 produced for a given O_2 flow. This would only be important if the detector is operated in a region where (13) is important and the signal thus gained is significant.

At this point one might be tempted to optimize an NO detector by using a very high speed pump and a large volumn reactor, but there is a third important factor, G in equation (10), that must also be considered. This factor represents the geometry of the photon collection system and the photomultiplier characteristics. These have been studied by varying the reactor design and by changing photomultiplier tubes.

The goal of good reactor design is to mix the entering flows of NO and O_3 very quickly and efficiently and then allow them to react as near the window to the photomultiplier as possible. This is because chemiluminescence is a diffuse source and cannot be focused by lenses or mirrors onto the photocathode. Also, as the

reactants flow through the reactor, the intensity of the light reaching the window falls off with the square of the distance. This is the reason one cannot continue to compensate for high pumping speed with large reactors. The ratio of τ_{react}/τ_{NO} may be kept large but some fraction of the reaction occurs far enough from the window to be effectively lost to detection.

The results in Table I with four different reactors support the above analysis. The best reactor was the glass reactor that mixed the reactants well in front of the window and allowed them to flow down the length of the reactor. Pumping them forward and out the side was 5-6 times less effective, and using a larger reactor with less efficient mixing gave only a third of the glass reactor signal. As already indicated, the brass reactor was too small, but its efficient mixing system and forward pumping might work well in a larger reactor. The best improvement in signal was produced by coating the glass reactor with Eastman Kodak reflectance paint which increased the signal by a factor of three.

The choice of photomultiplier tube is very important, but we did not have the resources to undertake any systematic study of this parameter. Ideally one would like to have a photomultiplier with a spectral response curve that maximally overlaps the chemiluminescence spectrum and one with a low dark current and noise. On the basis of spectral overlap, most photomultipliers fall short of the NO_2^* emission which peaks at 1200 nm. The ERMA-III response of the RCA 8852 photomultiplier extends about as far into the

infrared as any (900 nm) except the S-1 response of the Amperex 150 CVP, which extends to 1080 nm. This is shown in Table I by an order of magnitude increase in signal using this latter tube with the brass reactor. However, at its best, the S-1 photomultiplier has a dark current 45 times larger than the ERMA-III.

For maximum detector sensitivity for NO samples at ppb concentrations, one must be concerned about the background noise of the photomultiplier, and the important characteristic is the signal/noise ratio of the tube. The noise was such a strong function of cooling efficiency for the S-1 response photomultiplier that its signal/noise ratio varied from 1-7 X 10^4 to less than 10^3. The ERMA-III response photomultiplier has the best signal/noise ratio for the reflectance painted glass reactor of 6 X 10^4, and it seems to be the better of the two for use in an NO detector. It should be noted in Table I that one can increase the signal by increasing the operating voltage of the photomultiplier, but the noise is increased by the same factor and the signal/noise ratio remains about the same.

We can now summarize the choice of parameters for the optimization of the signal in an NO detector. They will be somewhat different for a detector designed to measure atmospheric NO where there is an infinite sample of gas available than for a detector designed to measure the NO concentration in a kinetics experiment or in a smog chamber where the amount of sample is finite and one may want to disturb the gases as little as possible.

First one should maximize the pumping speed within the constraints of being able to supply enough reactants to keep the

reactor pressure in the plateau region such as in Figures 2 and 3. For atmospheric sampling one does not care if the fall-off in pumping efficiency of the system comes at high pressures because one can supply enough sample to keep the pressure above this point. For laboratory sampling, however, one wants to have a high speed pumping system that falls off at a very low pressure so only a minimum of sample is required to keep the reactor pressure in the plateau region.

Secondly, one should choose a reactor that is large enough to keep the residence lifetime, τ_{react}, large compared to the reactive lifetime, τ_{NO}. There is a compromise between maximizing pumping speed and minimizing τ_{react}/τ_{NO} because the signal intensity decreases by a factor of the inverse of the distance squared of the excited molecules from the photomultiplier, and there may be an upper limit to the usable pumping speed unless one can lower τ_{NO} by increasing the ozone flux into the reactor.

Thirdly, reactor design should provide rapid efficient mixing as close to the window as possible. Furthermore, the walls of the reactor should be made as reflective as possible by coating with reflectance paint. It is difficult to put a mirror deposit on the inside of the reactor because of the large amount of ozone passing through it.

Finally, choose a photomultiplier with an extended response into the infrared that has a low dark current and low noise. One might be tempted to choose a photomultiplier with a larger diameter photocathode, in order to collect more light, but the noise increases as the square of the radius and one does not necessarily improve the signal/noise ratio. Ultimately the quality and characteristics of

the photomultiplier may be the most important factor in extending the sensitivity of an NO detector to lower NO concentrations.

Credit

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